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Modern Agriculture and Nanotechnology

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Abstract: Globally, many countries have identified the potential of nanotechnology in the agricultural sector. Therefore, they are investing significant funds into nanotechnological research. Developing countries also adopt their own nanotechnology programmes specifically focused on applications in agriculture. The development of nanotechnology in the long run is expected to emerge as an economic driving force in the agricultural industry.

Nanoproducts have been used recently in developing smart agricultural systems. For instance, nanosensors are used to identify plant health issues before they become visible. Sensors can respond to different situations by taking appropriate remedial action or they can alert the farmer to the problem. In this way, these smart devices act as both a preventive and an early warning system. Controlled and targeted drug delivery to specific tissues and organs has become highly successful, enabling high-precision treatment of different diseases such as cancer in animals. Researches have been underway on developing different technologies to create a system for the controlled release of fertilizers and pesticides aimed at enhancing their uptake by the plant. Technologies such as encapsulation and controlled release methods have revolutionized the use of pesticides and herbicides. In the near future, nanostructured catalysts will be available and they will increase the efficacy of pesticides and herbicides, allowing lower rates to be applied. The above investigations are also aimed at reducing environmental pollution and making agriculture more environmentally friendly.

The Faculty of Agronomy in Cacak has studied the electrochemical synthesis and characterization of nanocrystalline powders of alloys for their potential application in many fields of technical science, agricultural production and food industry.

Key words: nanotechnology, agriculture.

Introduction

Nanotechnology is an interdisciplinary field of research and development in chemistry, physics, biology and technical sciences (Roco *et al*. 1999). The development and use of nanotechnology may revolutionize the world, enabling the

production of novel substances through manipulations at the atomic and molecular levels. The development of this field will facilitate correlation between the macroscopic properties and structure of a substance within plant- and animal-derived biological materials (Kulzer *et al*. 2004). It is believed that the development of nanotechnology will enable scientists only to group atoms into structures with desired properties (Huang *et al*. 2001, Hoosian *et al*. 2005, Dutta and Hofmann 2004, Vayssiers *et al*. 2001). Nanotechnology products, due to their unique physical and chemical properties, have already been widely used in information technologies, telecommunication industry, medicine, automatics industry, chemical industry, environmental protection, as well as in agriculture and food industry (Liu *et al*. 2003). This is why more than 40 countries have adopted long-term national programmes of fundamental and applied research in nanotechnology.

Investments into the scientific research in this field are rapidly growing and, accordingly, the number of nanostructured products increases proportionally with the rising investment growth rate. The world market for nanotechnology-based products is expected to reach 1 billion dollars by 2015.

Modern agriculture makes use of computers and global satellite systems to measure highly localized environmental conditions and precisely identify the nature and location of problems (www.nano.gov, www.hkc22.com/nanofood.html). By using centralized data, seeding, fertilizer, chemical and water use can be fine-tuned to lower production costs and potentially increase production.

Globally, many countries have identified the potential of nanotechnology in the agricultural sector and are investing significant funds into nanotechnological research. For example, most funds in the USA are being invested in applied research. Distribution of projects by different fields of agriculture and food tehnology is given in Figure 1.

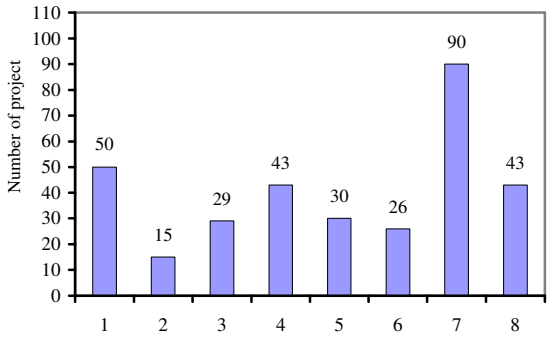


Fig. 1. Number of projects in different fields of agriculture in the USA: 1-biosensors; 2-environmental protection; 3- agricultural incentives; 4-pathogen detection; 5-plant and animal production; 6-veterinary medicine; 7-biofood and 8-nano-bioindustrial products.

Certain nanomaterials can control the amount of growth hormones used in livestock diet and thus increase livestock production. Smart sensors and smart delivery systems will help the agricultural industry combat viruses and other

crop pathogens. Nanomaterials are being developed to enable more effective and safer use of pesticides and fertilizers by controlling the time and location of their delivery. Early pathogen detection is of vital importance for medicine, agriculture, military and food industries and environmental protection. Bacteria, the causal agents of many diseases and food contamination, are identified by organic dyes (biolabels). Organic dyes are expensive and their fluorescence intensity decreases over time. Luminescent nanocrystals can be successfully used as bacteria identifiers. The luminescence of these identifiers is more effective than that of organic dyes. Their emission spectrum is symmetric and narrower, being dependent on particle size and particle composition (Alocilja and Radke 2003). Su and Li (2004) have developed a rapid *E. coli* detection method employing nanoparticles as fluorescent labels. There are efforts underway to develop nanomaterials to be used for simultaneous detection and destruction of pathogens in animals.

Controlled Environmental Agriculture (CEA) is an advanced and intensive form of agriculture. Plants are grown within a controlled environment so that horticultural practices can be optimized. Nanotechnology devices for CEA could improve the grower's ability to determine the optimum time of harvest for the crop, the vitality of the crop and food security issues, such as microbial or chemical contamination.

Nanotechnology can also be used to purify water. The use of a product that contains lanthanum nanoparticles in ponds and swimming pools can effectively remove phosphates, resulting in preventing the growth of algae. This product is expected to benefit commercial fish ponds which spend huge amounts of money to remove algae.

One of the major roles of nanotechnology-enabled devices will be the increased use of autonomous sensors linked into a GPS system for real-time monitoring (Sugunan *et al*. 2004). The union of biotechnology and nanotechnology in sensors will create equipment of increased sensitivity, allowing an earlier response to environmental changes. For example, nanoparticles can be engineered to trigger an electrical or chemical signal in the presence of a contaminant such as bacteria.

The Faculty of Agronomy in Cacak has been investigating the electrochemical synthesis of nanocrystalline powders of alloys and conducting other research, including the characterization of the obtained powders, i.e. identification of the chemical composition, structure, size and distribution of particles. It has also focused on the effect of operational and kinetic parameters of the electrochemical synthesis of powders on the electric and magnetic properties due to their potential use in many fields of technical science, agricultural production and food industry (Ribić-Zelenović *et al*. 2006, 2007, 2008, 2009, Ranđić *et al*. 2006, Kalezić *et al*. 2008).

Materials and methods

Specific attention is being given to researches on the structure of nanostructured materials. The structure of the obtained powders is evaluated by:

- X-ray structural analysis
- differential scanning calorimetry method
- measurement of the temperature dependence of electrical resistivity
- measurement of the thermoelectromotive force

- measurement of magnetic permeability as a function of temperature.

The electrochemical deposition of the Ni-Mo powder was performed in a glass 2 dm^3 electrochemical cell provided with a special compartment for a Lugin-capillary saturated calomel electrode. The anode was an 8 cm^2 platinum plate and the cathode was a 4.5 cm^2 titanium plate. The cell was located in the thermostat. The operating temperature was 298 ± 1K. The solution was prepared with p.a. chemicals (Merck) and triple-distilled water. The solution composition was: 0.035 mol dm^{-3} $NiSO_4 \cdot 7H_2O$; 0.007 mol dm^{-3} $Na_2MoO_4 \cdot 2H_2O$; 0.007 mol dm^{-3} NaCl and 0.7 mol dm^{-3} NH_4OH. The pH of the solution was maintained in the 11-11.5 range by adding ammonia solutions during the electrolysis. The Ni-Mo powder was obtained by galvanostatic deposition at a current density j=100 mA cm^{-2}. Upon electrolysis, the powder obtained was rinsed several times with triple-distilled water and then by 0.1% benzoic acid solution. Having been rinsed, the powder was dried at 360 K.

During the electrochemical measurements, standard electrical circuit composed of a programmer equipped with a potentiostat (RDE 3 POTENTIOSTAT Pine Instrument So. Grove City. Pennsylvania), digital voltmeters (Pro's Kit 03-9303C) and electrochemical cell were used.

The chemical composition of the obtained powder was determined using the PEKTAR-A.A.200-VARIAN atomic absorber.

X-ray diffraction (XRD) was conducted through a Diffractometer Philips PW e17e10 with CuK_α (α = 0.154 nm) radiation and a graphite monochromator. XRD data were collected in a step mode of 0.03º with collection time of 1.5 s/step. Scanning electron microscopy (SEM) was conducted by a JEOL.JSM 5300 supplied with a EDS-QX·2000S spectrometer.

The X-ray photoelectron spectroscopy (XPS) experiments were carried out using a ''SERIES 800 XPS'' Kratos Analitical. The Mg K_α line at 1253.6 eV was used for excitation in all casses. All measurements were referenced to the C 1s line binding energy of 285.0 eV.

Investigation of the electrical properties was made using 40x1.2x0.5 mm samples, obtained by powder pressing under a pressure of 100 MPa. Electrical resistivity was measured by the four-point method within the temperature interval of 293 K to 950 K. The measurements were made in the argon atmosphere.

Results and discussion

The phase structure of nickel-molybdenum alloy powders obtained at different current densities and from solutions of different nickel and molybdenum salt concentrations has been investigated by the X-ray diffraction method. A Rietvald diagram of a nickel-molybdenum powder is given in Figure 2. The diffractogram shows four well defined peaks for different planes of the face-centred cubic lattice, *FCC*.

The size distribution and shape of powder particles are dependent on deposition current density. Smaller particles are formed at higher current densities.

The figures obtained by scanning electron microscopy (SEM) show that two particle structures are formed: larger cauliflower-like particles and smaller

dendrite-shaped ones. A cauliflower-like particle of the nickel-molybdenum alloy powder obtained at a current density of j=180 mAcm^{-2} is given in Figure 3 (a). The dendrites have already grown on the particle surface. The central part of the SEM in Figure 3 (b) shows a particle that started to grow as a dendrite, and then, after a certain period of electrodeposition, transformed into a cauliflower.

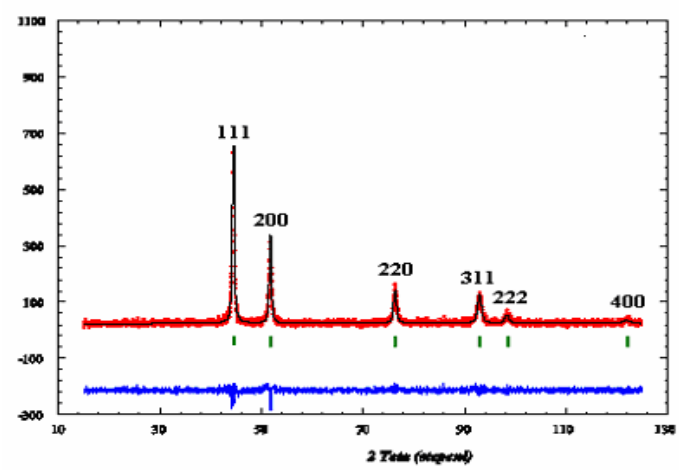
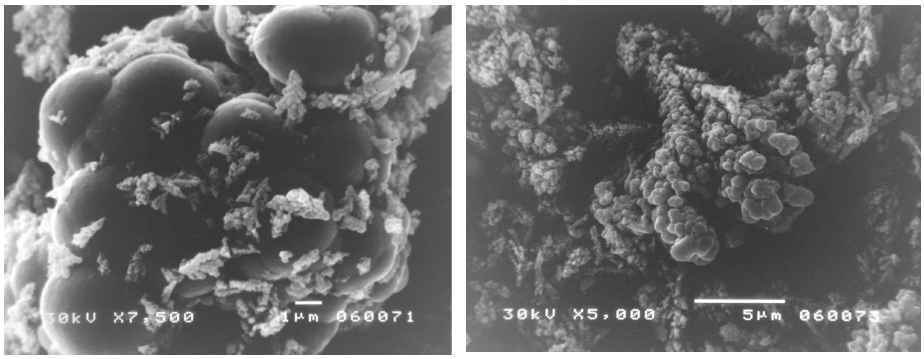


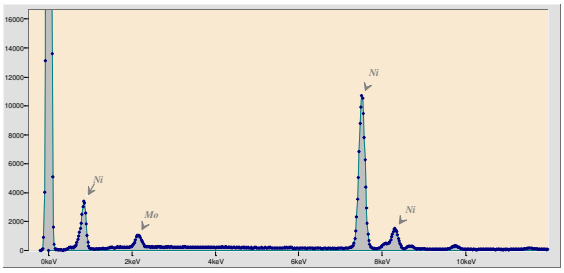
Fig. 2. A Rietvald diagram of the nickel-molybdenum powder obtained from the solution: 0.035 mol dm^{-3} $NiSO_4 \cdot 7H_2O$; 0.007 mol dm^{-3} $Na_2MoO_4 \cdot 2H_2O$; 0.007 mol dm^{-3} NaCl; 25% solution of NH_3 up to pH = 12 at T=298 K and j=180 mA cm^{-2}



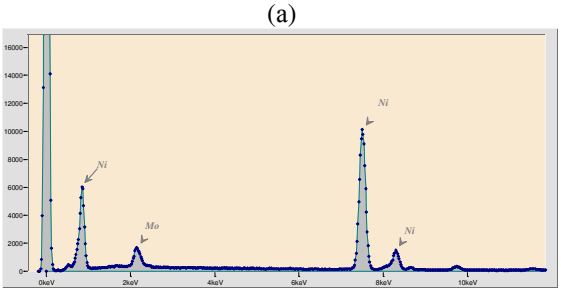
(a) (b)

Fig. 3. SEM photograph of the nickel-molybdenum alloy powder obtained at a current density of j = 180 mA cm^{-2}: (a) cauliflower-like particles and (b) dendrites.

The molybdenum content of the dendrites is different from that of the cauliflower-like particles. A semi-quantitative analysis of the EDS spectra, nickel-molybdenum alloy powders obtained at different current densities, reveals that the molybdenum content is lower in the dendrites than in the cauliflower-like particles (Figure 4).



(a)



(б)

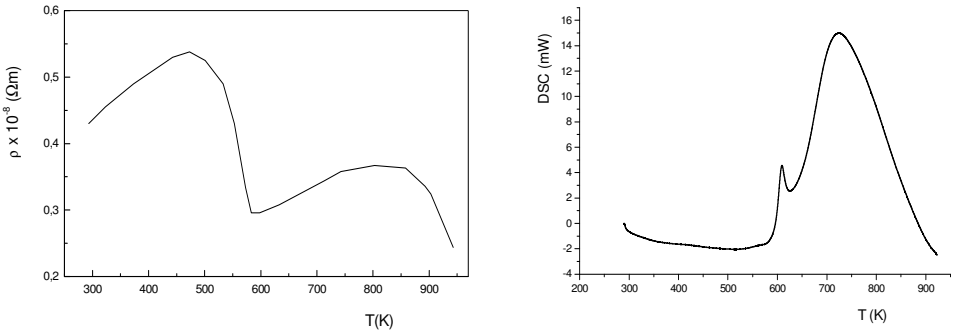
Fig. 4. EDS spectra of the Ni-Mo alloy obtained at a current density of j=180 mA cm^{-2}: (a) for dendrites and (b) for cauliflower particles.

The structural changes of the electrochemically obtained powders of the nickel-molybdenum alloys are also monitored by measurements of the temperature dependence of electrical resistivity (Figure 5, a). During heating of the powders obtained at a current density of j=180 $mAcm^{-2}$, the resistivity increases linearly with increasing temperature over the interval of 300 K to 450 K, indicating that structural changes in the alloys do not take place. In the 450 K to 580 K temperature interval, the resistivity decreases with increasing temperature. This suggests that structural relaxation occurs in the above temperature range. The high drop in resistivity within the temperature interval of structural relaxation results from defect annihilation, which induces an increase in electron numbers in the conduction zone.

The resistivity drop induces better contact between the powder particles. The figure shows that structural relaxation is followed by a linear increase in resistivity, which gradually slows down, reaching its maximum and, subsequently, decreasing with increasing temperature. These changes in electrical resistivity are due to:

- the crystallization of amorphous portion of the powder;
- crystal grain increases;
- dislocation density and microstrain decreases.

The obtained results on the measurement of the temperature dependence of electrical resistivity are correlated with the X-ray and DSC results (Figure 5, b).



(a) (b)

Fig. 5. Temperature dependence of electrical resistivity (a) and DSC (b) of the nickel-molybdenum alloy powder obtained at j=180 mA cm^{-2}.

Conclusion

Nanotechnology products are used to develop smart agricultural systems which identify plant health issues before they become visible and respond to different situations by taking appropriate remedial action. In this way, these smart devices act as both a preventive and an early warning system.

They can also be used in the controlled and targeted release of chemicals. Researches have been underway on developing different technologies to create controlled fertilizer and pesticide release systems that can respond to environmental changes. The use of nanotechnology-based products in agriculture ensures more effective water, pesticide and fertilizer utilization by the plant. The union of biotechnology and nanotechnology in sensors will create equipment of increased sensitivity, as nanoparticles can be engineered to trigger an electrical or chemical signal in the presence of a contaminant. This will allow an earlier response to environmental changes and make agriculture more environmentally friendly.

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NANOTEHNOLOGIJA U SAVREMENOJ POLJOPRIVREDI

- originalni naučni rad -

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Rezime

Mnoge zemlje u svetu su svesne mogućnosti koje pruža primena nanotehnologije u poljoprivrednom sektoru i ulažu značajna sredstva u istraživanja iz oblasti nanotehnologije. I u zemljama u razvoju, razvijaju se sopstveni nanotehnološki programi sa naglaskom na primenu u poljoprivredi. Predviđa se da će razvoj nanotehnologije, posmatrano u dugoročnom periodu, postati pokretačka ekonomska snaga u poljoprivrednoj industriji.

U novije vreme nanoproizvodi se koriste za stvaranje inteligentnih poljoprivrednih sistema. Nanosenzori se, na primer, primenjuju za identifikovanje problema vezanih za zdravlje biljke pre nego što oni postanu vidljivi. Senzori mogu da reaguju na različite situacije preduzimanjem odgovarajućih mera popravki ili mogu da upozore farmera na postojanje problema. Na ovaj način, ovi inteligentni proizvodi su i preventivni i upozoravajući sistemi. Danas se veoma uspešno ostvaruje kontrolisana i ciljna isporuka lekova u odredjena tkiva i organe i time omogućuje lečenje različitih bolesti sa velikom preciznošću, kao što su kancerogena oboljenja kod životinja. Veoma su aktuelna istraživanja različitih tehnologija za stvaranje sistema za kontrolisano oslobadjanje djubriva i pesticida u cilju njihovog efikasnijeg iskorišćavanja od strane biljke. Tehnologije poput kapsulacije i metoda kontrolisanog oslobadjanja, unele su radikalne promene u primenu pesticida i herbicida. Predviđa se da će u skorijoj budućnosti primenjivati nanostrukturni katalizatori za povećanje efikasnosti pestidica i herbicida, što će omogućiti unošenja manjih doza. Krajnji cilj ovih istraživanja je smanjenje zagadjenja životne sredine i ekološki prihvatljivija poljoprivreda.

Na Agronomskom fakultetu u Čačku istražuje se elektrohemijska sinteza i karakterizacija nanokristalnih prahova legura zbog mogućnosti njihove primenu u mnogim granama tehnike i različitim oblastima poljoprivredne proizvodnje i prehrambene industrije.